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PATENT SPECIFICATION

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(54) SILVER PLATING ELECTROLYTE

(71) We, SIEMENS AKTIENGESELLSCHAFT, a German Company of Berlin and Munich, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a cyanide-containing silver plating electrolyte and to its use in the electrolytic deposition of silver-graphite dispersion coatings.

Contact layers are often produced consisting of silver or a silver-copper alloy, e.g. $AgCu_3$, for use for example for relays. Such contact layers can be produced by powder metallurgical procedures or by electro-deposition. When used in relays, the layers are subject to heavy mechanical wear. In general, surface layers subject to mechanical stress, e.g. by friction, can be reduced by incorporation therein of graphite. Graphite-containing nickel or iron coatings have been described in an article published by D. Löffler, in Galvanotechnik (65) 1974, No. 5, page 360. These nickel or iron coatings are electrolytically produced and contain a non-metallic phase, in this case graphite, finely distributed as uniformly as possible, in a metal layer by deposition with the metal from acid baths.

According to the present invention there is provided an alkaline cyanide-containing silver plating electrolyte for electrolytic deposition of a silver/graphite coating, which electrolyte additionally contains from 10 to 100 g/litre of graphite having a particle size of from 1 to 10 μm, from 0.02 to 5 g/litre of one or more brightening agents for deposition of silver and from 0.05 to 2 g/litre of one or more wetting agents for use in an alkaline electrolyte.

Thin, graphite-containing silver surface layers of thickness less than 20 μm, if required, can be produced by use of such an electrolyte in an electrolytic procedure. Such surface layers are suitable for use in relay contacts and cannot be produced by powder metallurgical methods.

The graphite-containing surface layers produced electrolytically using an electrolyte according to the invention are smooth and uniform. The graphite is present in the silver-graphite disperaion coating in an extremely fine and uniform distribution. The graphite content of the silver layer will, of course, depend on the particular use to which the silver layer is to be put, but, in general, graphite contents of from 0.1 to 3% by weight can be readily produced. The silver-graphite coatings generally have a hardness (HV 0.05) which loes in a range from 700 to 1000 N/mm^2.

Silver-graphite dispersion coatings produced using the bath according to the invention show an excellent resistance to abrasion. Abrasion tests with silver/graphite coatings which contain from 1.0—1.5% by weight of graphite, have shown that such dispersion layers undergo wear by amounts one tenth or even less of the wear encountered with pure silver or silver-copper alloy layers or coatings under the same conditions.

This invention also provides a process for producing, on a metal substrate, a silver coating having graphite dispersed therein which comprises electrodepositing the silver/graphite from an electrolyte according to this invention, preferably at a temperature of from 25 to 30°C and preferably with a cathodic current density of 1 to 5 A/dm^2.

A silver electrolyte which is particularly suitable for use in the present invention contains potassium silver cyanide, potassium cyanide and potassium carbonate. Fine-grain graphite is also to be present in the silver electrolyte, which graphite is held in suspension during the deposition procedure by circulating the electrolyte in the container in which electrodeposition is being effected.

Brightening agents used in the electrolyte are preferably chosen from Turkey red oil, carbon disulphite, sodium xanthate, dithiocarbamate, thiothiazolidine, sodium thiosulphate, ammonium thiosulphate and sodium selenite. Sodium xanthate and sodium selenite are particularly suitable.

The wetting agent which is used in the electrolyte is preferably chosen from Turkey red oil, sulphonated oleate esters, fatty alcohol sulphonates, for example sodium lauryl sulph-

onate, and alkylaryl sulphonates, for example dibutyl-sodium naphthalene sulphonate. Sodium lauryl sulphonate has proved to be particularly suitable.

Silver/graphite dispersion coatings may be obtained using an electrolyte according to this invention on, for example, steel, copper or copper alloys, aluminium, nickel, molybdenum or tungsten. If desired, the substrate metal may be subjected to a pretreatment, for example by deposition of an intermediate layer, for example of nickel deposited electrolessly.

As will be appreciated from the foregoing, Turkey red oil may be used for its properties as a brightening agent, and/or as a wetting agent and may thus be used alone or with one or more other brightening agents and/or one or more other wetting agents.

In such a case, the amount of substance(s) acting as wetting agent and/or brightening agent should total 0.07 to 7 g/litre.

Graphite-containing surface layers produced using an electrolyte embodying this invention may be used as contact layers in general. They can for example be used for relay contacts or also for other purposes, for example for lining bearings.

The following Examples illustrate this invention:

EXAMPLE 1

Metal articles were electrolytically coated with a silver layer having graphite dispersed therein after a pretreatment comprising pickling and degreasing. The electrolyte had the following composition:

Potassium silver cyanide $K[Ag(CN)_2]$	46 g/l
Potassium cyanide, KCN	75 g/l
Potassium carbonate, K_2CO_3	20 g/l
Graphite, grain size 1—5 μm	20 g/l
Sodium xanthate	0.075 g/l
Turkey red oil	5 g/l
Sodium lauryl sulphonate	0.17 g/l

The electrodeposition was carried out at a temperature of 30°C using a cathodic current density of 2 A/dm². The silver/graphite layer was produced in a layer thickness of 15 μm and had a graphite content of 0.4% by weight.

EXAMPLE 2

The procedure of Example 1 was repeated using an electrolyte having the following composition.

Potassium silver cyanide $K[Ag(CN)_2]$	46 g/l
Potassium cyanide, KCN	75 g/l
Potassium carbonate, K_2CO_3	20 g/l
Graphite, grain size 1—5 μm	50 g/l
Dithiocarbamate	0.1 g/l
Sodium lauryl sulphonate	0.45 g/l

In this case a silver/graphite layer having a layer thickness of 15 μm, as before, was produced, the layer having a graphite content of 1.0% by weight.

EXAMPLE 3

The procedure of Example 1 was again repeated using a third electrolyte and employing a cathodic current density of 1 A/dm, while keeping the working temperature at 30°C. The electrolyte had the following composition:

Potassium silver cyanide $K[Ag(CN)_2]$	46 g/l
Potassium cyanide, KCN	75 g/l
Potassium carbonate, K_2CO_3	20 g/l
Graphite, grain size 1—5 μm	75 g/l
Sodium selenite	2 g/l
Sodium lauryl sulphonate	0.7 g/l

The silver/graphite coating was again obtained in a layer thickness 15 μm, the layer having a graphite content of 2.3% by weight.

WHAT WE CLAIM IS:—

1. An alkaline cyanide-containing silver plating electrolyte for electrolytic deposition of a silver graphite coating, which electrolyte additionally contains from 10 to 100 g/litre of graphite having a particle size of from 1 to 10 μm, from 0.02 to 5 g/litre of one or more brightening agents for deposition of silver and from 0.05 to 2 g/litre of one or more wetting agents for use in an alkaline electrolyte.

2. An electrolyte as claimed in claim 1, which contains potassium silver cyanide, potassium cyanide and potassium carbonate.

3. An electrolyte as claimed in claim 1 or 2, wherein the brightening agent(s) is/are selected from dithiocarbamate, sodium xanthate, sodium selenite and Turkey red oil.

4. An electrolyte as claimed in any one of the preceding claims, wherein the wetting agent is/are selected from Turkey red oil, sulphonated oleate esters, fatty alcohol sulphonates and alkylaryl sulphonates.

5. An electrolyte as claimed in claim 4, wherein the wetting agent is sodium lauryl sulphonate.

6. An electrolyte as claimed in any one of the preceding claims, which contains Turkey red oil as both brightening agent and wetting agent and optionally at least one other brightening agent and/or at least one other wetting agent, the amount of compound(s) acting as wetting agent(s) and/or brightening agent(s) totalling from 0.07 to 7 g/litre.

7. An electrolyte for electrolytic deposition of a silver/graphite coating, substantially as described in any one of the foregoing Examples.

8. A process for the production on a metal substrate of a silver coating having graphite

dispersed therein, which comprises electrodepositing the silver/graphite from an electrolyte as claimed in any one of the preceding claims.

9. A process as claimed in Claim 8, wherein electrodeposition is effected at a temperature of from 25 to 30°C.

10. A process as claimed in Claim 8 or 9, wherein electrodeposition is effected at a cathodic current density of 1 to 5 A/dm².

11. A process as claimed in any one of Claims 8 to 10, wherein silver/graphite is electrodeposited on a surface formed of steel, copper or a copper alloy, aluminium, nickel, molybdenum or tungsten.

12. A process as claimed in any one of Claims 8 to 11, wherein a silver/graphite layer having a thickness of less than 20 μm is produced.

13. A process for the production of a silver/graphite coating on a metal substrate, substantially as described in any one of the foregoing Examples.

14. A metal substrate on which a silver/graphite coating has been produced by the process claimed in any one of Claims 8 to 13

15. A silver/graphite coated metal substrate as claimed in Claim 14, which is a relay contact.

16. A silver/graphite coated metal substrate as claimed in Claim 14 or 15, wherein the silver coating containing graphite has a hardness (HV 0.05) of from 700 to 1000 N/mm².

17. A silver/graphite coated metal substrate as claimed in any one of Claims 14 to 16, wherein the coating contains from 0.1 to 3% by weight of graphite.

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